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<p>(71) Applicant <b>Imperial Chemical Industries PLC</b>  (Incorporated in United Kingdom)  <b>Imperial Chemical House, Millbank, London SW1P 3JF</b></p> <p>(72) Inventors <b>Bruce Murray McIntosh</b> <b>Frederic Neil Cogswell</b></p> <p>(74) Agent and/or Address for Service <b>Raymond Hulse,</b> <b>Imperial Chemical Industries PLC, Legal Dept: Patents,</b> <b>PO Box 6, Bessemer Road, Welwyn Garden City,</b> <b>Hertfordshire AL7 1HD</b></p>	<p>(58) Field of search <b>B5B</b> <b>Selected US specifications from IPC sub-class D01F</b></p>

(54) **Filamentary yarn and film of an aromatic polyetherketone**

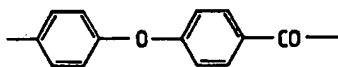
(57) A process of melt spinning a yarn or of extruding a film from an aromatic polyetherketone in which prior to spinning or extruding, there is admixed with the polyetherketone polymer in excess of 2% by weight of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film.

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## SPECIFICATION

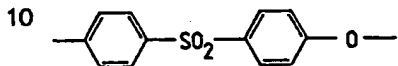
## Filamentary yarn and film of an aromatic polyetherketone

- 5 This invention relates to the melt spinning of mono- and multi-filament yarns and to the  
extrusion of a film from an aromatic polyetherketone and more particularly an aromatic polyether-  
etherketone. 5
- We have found it possible to produce extruded products, more particularly melt spun textile  
filaments, of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone  
10 by conventional melt spinning techniques. This involves melting either a powder or granules of 10  
the polymer at between 350°C and 400°C and, using a metering screw or pump, passing the  
melt to a filter pack where the melt is filtered through graded sand, graded gauzes or sintered  
metal having a pore size down to about 25 microns. The molten polymer is then extruded  
15 through a spinneret at 370°C to 400°C into filaments which are drawn down in a controlled 15  
cooling environment. Subsequent processing may involve a reheating of the filaments above  
150°C and the drawing of the filaments by a factor of about 3 to complete orientation of the  
filaments. Film can be produced in a similar manner using a slot die rather than a spinneret.
- However with such techniques we have found it becomes increasingly difficult to produce  
20 filaments 'raining' from the spinneret occurs causing very short lengths of increased diameter to 20  
occur in the spun filaments at draw down and it is suspected that the breaks which occur both  
in the extrusion draw down and in the orientation zone are associated with these discontinuities.  
This, we have found, limits the fineness of the filaments of polyetheretherketone that can be  
produced to between 50 and 100 microns depending on the effectiveness of the filtration used.
- 25 In the production of thin films using a slot die instability of the melt curtain edge occurs at 25  
thicknesses of about 20 microns and below.
- In European Patent Application No 83304022.3 there is described a process of producing a  
fibre-reinforced composition comprising passing a plurality of continuous filaments of, for  
30 example, glass or carbon, through a melt comprising a mixture of a thermoplastic polymer, such 30  
as an aromatic polyetheretherketone, and a plasticiser which is thermally stable at least up to  
the temperature of the melt and having volatility characteristics such that the plasticiser can be  
volatilised from the composition below the decomposition temperature of the thermoplastic  
polymer but has sufficiently low volatility at the temperature of the melt to plasticise the polymer  
and provide a melt of reduced viscosity compared with the melt viscosity of the polymer alone.
- 35 We have now found that the addition of substantial quantities of a plasticiser as used in the 35  
process described in European Patent Application No 83304022.3 to a polyetherketone and  
more particularly a polyetheretherketone before it is melt spun gives rise to a very much more  
regular extrusion for otherwise similar processing conditions. In addition work done by the  
extruder screw is reduced considerably and it is possible to reduce the extruder temperature.
- 40 Consequently we have found using the modified process that filament diameters in the range 20 40  
to 50 microns can be produced without frequent filament breaks.
- According to the invention, therefore, we provide a process of melt spinning a mono- or multi-  
filament yarn or of extruding a film from an aromatic polyetherketone and more particularly an  
aromatic polyetheretherketone in which, prior to spinning or extruding, there is admixed with the  
45 polyetherketone polymer a substantial proportion of a plasticiser which is thermally stable at the 45  
temperature of the melt and provides a melt of reduced viscosity compared with the melt  
viscosity of the polymer alone such plasticiser having volatility characteristics such that though  
some of the plasticiser volatilises from the spun yarn or extruded film during the process, more  
than 1% by weight of the plasticiser remains in the spun yarn or extruded film.
- 50 It will be realised, therefore, that in the process all of the plasticiser is not removed the yarn 50  
or film and indeed, for certain applications, there are advantages to be gained from this.
- We also provide a melt spun mono- or multi-filament yarn or an extruded film of an aromatic  
polyetherketone and more particularly an aromatic polyetheretherketone containing in excess of  
1% by weight of a plasticiser having the above defined stability and volatility characteristics.
- 55 Such a yarn or film can be readily converted into a porous yarn or film by an elevated heat 55  
treatment process between 250°C and 300°C preferably under vacuum.
- According to another aspect of the invention, therefore, we provide a porous yarn or film of  
an aromatic polyetherketone and more particularly an aromatic polyetheretherketone.
- By the term "substantial" which is used in connection with the proportion of plasticiser which  
60 is admixed with the polyetheretherketone polymer we mean that in the melt prior to spinning or 60  
extruding there is present in excess of 2% by weight of the plasticiser.
- Suitable polyetherketones for use in the invention include those which contain the recurring  
unit (I):



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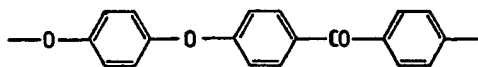
Such polymers are disclosed, inter alia, in British patent specification 1 414 421 which describes such polymers containing the unit (I) as the sole repeating unit or in conjunction with the repeating unit (II):



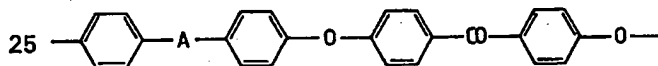
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A preferred polyetheretherketone having the repeating unit (III):

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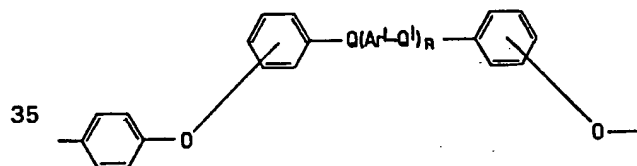
either alone or in conjunction with other repeating units is disclosed in European patent publication No 1879. The other repeating units present in the polymers described in the European application may be of the repeating unit (IV):



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where A is a direct link, oxygen, sulphur,  $-SO_2-$ ,  $-CO-$  or a divalent hydrocarbon radical. The repeat units may also be of formula (V):

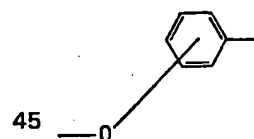
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where the oxygen atom in the sub-units:

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are *ortho* or *para* to the groups Q and Q', Q and Q' which may be the same or different are  $-CO-$  or  $-SO_2-$ , Ar' is a divalent aromatic radical, and n is 0, 1, 2 or 3.

The plasticisers which are suitable for use in the invention are materials which are thermally stable at the melt temperatures of polyetheretherketone and which can be partially volatilised from yarns or films during the production thereof in accordance with the invention process. Apart from that the plasticisers used will essentially have the capability of providing a plasticised polymer melt of lower melt viscosity than the polymer itself. Suitable plasticisers having these characteristics are found in the classes aromatic ketones, aromatic sulphones and aromatic esters. Typical plasticisers in these classes are diphenyl sulphone, ditolyl sulphone, benzophenone, phenyl benzoate and benzyl benzoate.

The plasticiser and polymer may be admixed by any conventional technique. For example, a mixture may be achieved:— by dry blending the polymer and the plasticiser, by compounding in a screw extruder, by coating granules of the polymer with a solution of the plasticiser and volatilising the solvent from the coated granules or in suitable cases by adding the plasticiser in the course of producing the polymer.

As mentioned above the mixture of the plasticiser and the polymer will have a reduced melt viscosity compared with the melt viscosity of the polymer alone. Furthermore we have found that the addition of the defined plasticiser serves to greatly reduce the tendency of the melt to

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